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WO 03/009991 A1

(54) Title: PRODUCTION OF CONTINUOUS POLYACRYLONITRILE FIBERS

(57) Abstract: A process and apparatus for the production of polyacrylonitrile (PAN) polymer fibers from a polyacrylonitrile polymer, wherein a polyacrylonitrile polymer that comprises 90 weight percent or more polyacrylonitrile, optionally mixed with from about 30 to about 50 weight percent, based on the weight of the polymer, of a fugitive plasticizer, is heated, provided to an extruder in liquid form, extruded to form polyacrylonitrile fibers, and the fibers, immediately after the extrusion, are cooled, preferably in an air-cooled manifold, to a temperature of from about 110 to about 135° C. Fibers so produced have increased tensile strength, and thus are useful for more purposes, than typically produced polyacrylonitrile fibers.

## PRODUCTION OF CONTINUOUS POLYACRYLONITRILE FIBERS

[01] This application claims the priority of United States provisional patent application no. 60/307,630 filed July 24, 2001. The disclosure of said provisional patent application is incorporated herein by reference for all legal purposes capable of being served thereby.

### BACKGROUND OF THE INVENTION

[02] This invention resides in the field of polymeric fibers, particularly polyacrylonitrile fibers, and processes for their manufacture.

[03] The acrylic fibers industry, a 60-year old enterprise, has witnessed little growth over the past decade, in part because such fibers are produced from a polyacrylonitrile (PAN)/solvent solution. However, currently, hot melt heat-processable thermoplastic polymers are preferred for many uses, particularly because they can be produced at lower cost. Despite this growth problem, the acrylic fibers industry produces about 5.3 billion pounds of fibers annually across the globe. This is due to such fibers having desirable properties such as a close likeness to wool in feel or "handle", high tensile strength, long resistance to ultraviolet degradation, high temperature resistance, and resistance to most common chemicals. Even more important is the singular ability of PAN fibers to be transformed by oxidation and carbonization into PAN carbon fiber, the relatively new high tech material that is ten times stronger than steel, pound for pound.

[04] Thermoplastic polymers such as polyester, nylon and polypropylene are relatively easy to process into fibers. They therefore possess a primary advantage over PAN fibers, even though they may not have some of the same uses and properties, such as transformation to carbonized fibers. To form fibers the thermoplastic polymers are simply melted by heat into an extruder, pumped to a spinneret and spun into fibers through the holes in the spinneret. While still warm, the fibers can be tensilized or stretched to the desired degree using a convenient speed, and are then spooled or wound up.

[05] Non-thermoplastic polymers such as PAN and rayon cannot be converted to fibers by simple heat processing. Instead, these polymers are dissolved in a suitable solvent and the solution is pumped to the spinneret as a syrup. The pump pressure forces the syrup through the holes in the spinneret to form the fibers.

[06] Acrylic fiber polymer is based on non-thermoplastic acrylonitrile (AN) monomer typically comprising 85% by weight of AN monomer copolymerized with 15% by weight of "neutral" co-monomers such as ethyl acrylate, methyl methacrylate, and vinyl acetate. Such co-monomers impart sites on the fiber to which coloring agents can attach, as well as higher tensile properties for tensilizing (stretching) the fibers as they are formed at high speeds into continuous filaments. They also provide higher tensile strength for high-speed fiber production. However, when the PAN fiber is to be used to make PAN carbon fibers, the co-monomers provide a disadvantage. Oxidation and carbonization of them requires a slow buildup of heat, for a time of from 30-120 minutes or longer, to prevent the fibers from overheating by internal means, with a resulting loss of cohesive property values ("runaway" heat rise).

[07] These problems can be overcome by use of a process such as described in U.S. Patent No. 5,304,590, which is hereby incorporated herein by reference. This patent discloses a process wherein PAN polymers having AN monomer levels of from 90 to 99.6 % by weight, and containing no neutral co-monomers, can be melt fused in a standard plastics extruder at high-speed running rates, into a clear polymeric melt that performs as though it were a thermoplastic compound. One example cited is a PAN polymer comprised of 99.5 % by weight AN monomer, polymerized with an FDA approved chain extender cross-linking agent comprising the other 0.5 % by weight of the polymer. Such chain extender cross - linking agent eliminates the need for the neutral co-monomer. The use of an efficient molecular chain extender cross - linking agent enables such PAN to be made into biaxially oriented (stretched in both the machine direction [MDO] and the transverse direction [TDO]) thin films without fibrillating, while imparting high flexibility to the films, without brittleness. It also provides superior mechanical, electrical and barrier properties by allowing a greater amount of AN monomer to be available in both films and fibers.

[08] In addition, using polymers produced by the process of U.S. Patent No. 5,304,590, enables reduction in the amount of fugitive plasticizer from 70 to only 40 % by weight of the PAN polymer, which materially reduces the cost of manufacture of these melt fused PAN fibers while at the same time increasing the amount of AN monomer by almost 15% by weight.

[09] In the process of U.S. Patent No. 5,304,590, the PAN polymer used for melt fusion is washed and rinsed thoroughly, with its moisture adjusted to about 0.5 % by weight. The

PAN is dry blended with ethylene carbonate (EC) as a fugitive plasticizer. The mixture is fed to a standard low shear vented extruder that fuses the materials into a smooth polymeric melt at relatively low temperature for pelletizing, precursor sheet for thin biaxial film preparation, or fiber production. Production process heat volatilizes EC from the formed product, and it is ducted to a cooling tower, where the EC changes at 95° F (35°C) into small crystals that may be used in subsequent production runs.

[10] However, when attempting to make acrylic fibers formed by a spinneret from such a PAN polymer, it was found that such filaments tended to break too readily under the extrusion temperatures required for high-speed extrusion. This may be due to the lack of thermoplastic types of "neutral co-monomers".

[11] It thus would be desirable to provide PAN fibers from PAN polymer, and particularly from PAN produced by melt fusion, in which the fibers possessed a greater tensile strength.

#### BRIEF SUMMARY OF THE INVENTION

In brief, the invention comprises an improvement in a process for the production of polyacrylonitrile fibers from a polyacrylonitrile polymer wherein a polyacrylonitrile polymer that comprises 90 weight percent or more polyacrylonitrile, optionally mixed with from about 30 to about 50 weight percent, based on the weight of the polymer, of a fugitive plasticizer, is heated, provided to an extruder in liquid form, and extruded to form polyacrylonitrile fibers, the improvement comprising,

cooling the fibers, immediately after the extrusion, to a temperature of from about 110 to about 135° C.

[12] In another aspect the invention comprises a cooling manifold through which the fibers are passed, and in which the cooling step is carried out.

[13] Other aspects of the invention will become apparent to those skilled in the art from the description that follows.

#### BRIEF DESCRIPTION OF THE DRAWING

[14] Figure 1 generally depicts a cooling manifold as used in this invention.

## DETAILED DESCRIPTION OF THE INVENTION

[15] PAN polymer is a white, fine powder that is dissolved in a polar solvent such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) or similar solvents or combinations of proprietary types. Dissolution is typically 70% by weight solvent to 30% by weight PAN. This provides a hot syrup which in conventional fiber production is pumped to a spinneret (a die having a multitude of orifices through which the syrup exits the spinneret) thus forming the filaments. Generally, the diameter of such filaments ranges from 0.015" to 0.002". The filaments are tensilized by passing them around a series of rollers, each running at a faster rate than the one before it, thereby causing the filaments to have their molecular chains aligned in the machine direction, which increases tensile properties. The degree of stretching thins the filament to the desired diameter. The filaments are given selected types of treatments for specific end use enhancements, spooled and sold. The solvent is removed from the fibers by either "dry spinning" by passing them through a heated chamber while tensilizing, or by "wet spinning"; i.e., submerging the filaments in a solvent - water trough to coagulate the fibrils by washing, then drying them, as they are tensilized. The solvent volatilization vapor is ducted to a recovery system, condensed, purified, and reused in subsequent batches.

[16] In losing its solvent during production, the circular fiber profile collapses into many odd profile shapes (boomerang, dog bone, etc.) giving the fibers great spring or wool-like hand. The departing solvent also causes the formation of microscopic pores in the fiber that allow the fiber to "breathe" or absorb moisture for wearing apparel comfort. Thermoplastic fiber polymers do not have this valuable characteristic.

[17] Melt fused PAN polymers dry blended with EC fugitive plasticizer having a ratio mixture of 60% - 40% by weight respectively, are optimally extruded at 160-175°C (320 - 347°F). According to this invention, it has been found that by reducing the temperature of the filaments to 110 - 135°C (248 - 275°F) immediately after extrusion, their tensile strength materially increases, to provide the necessary tensile strength to carry out the tensilizing function at high speed. A mechanical means of reducing such filament temperature rapidly and accurately to achieve higher tensile properties, is a key element to this invention. The preferred temperature, regardless of fiber diameter, is 120°C.

[18] The lower temperature level allows the amount of EC plasticizer to remain at a high level in the polymer melt allowing for easy and uniform stretching. Reinforcing this process is the contribution of having a PAN polymer richer in AN monomer available to stretch many times its extruded length to diameter. The PAN polymer preferred has a beginning average molecular weight of 80,000, which propagates to 230,000 during processing. Presently used PAN polymers typically have a starting molecular weight of 30,000, which remains at or near such level throughout the process, when making fiber from a solution of PAN and solvent.

[19] A separate high nitrile PAN polymer, especially tailored as a precursor for the production of PAN carbon fiber, which cannot be melt fused but contains no neutral comonomers, can also benefit from the present invention, as it too needs protection from too frequent fibril breakage for high speed tensilizing.

[20] This invention consists of an oven into which formed fibrils from either the melt fusion process, or from the PAN/solvent solution process, passes into a perfectly controlled environment to optimize the fibril tensile properties for downstream treatment of such fibrils.

[21] Combined with use of the melt fusion process of U. S. Patent 5,304,590 for non-thermoplastic PAN polymers, this invention can materially reduce the cost of production of PAN-based fibers, thereby permitting PAN to better compete with thermoplastic polymers. This is especially true for precursor PAN fibers for PAN carbon fiber production. PAN is the only polymer which can be oxidized and carbonized into carbon fibers with superior properties, to meet the challenge of the industry need to reduce the cost and improve the quality of such PAN carbon fibers and their anticipated high tech growth.

[22] The temperature reduction feature of this invention causes the newly formed fibers to reach a steady state with respect to being non-sticky, holding a shape and contour definition, and a greatly enhanced tensile strength, without engaging the chain extender cross-linking agents of the polymer. At the same time, the level of EC plasticizer at such stage of production remains within a percentage or two of its level when exiting the spinneret, thereby capable of high performance as a plasticizer for the tensilizing steps of production to follow.

[23] There are numerous design possibilities for the many spinneret styles to be encountered in setting up this mechanism for cooling PAN fibers just out of the spinneret. One suitable fiber take-off design would have holes that match each fiber exit hole from the spinneret, to allow each fiber to pass through such holes in the form of tubes made from an appropriate material such as stainless steel. These tubes would extend from the manifold's

top side adjacent to the spinneret, to the bottom side of the manifold in the interior space between the top and bottom interior surfaces. Connected to the manifold would be entry and exit ports to transport a fluid medium such as water, oil, ethylene glycol or a combination of materials for optimum functionality. Cooled air may also be used as a coolant medium in such a manifold chiller device. By controlling the cooling media temperature coordinated with the fiber diameter and rate of throughput passage of the fibers, exact melt temperature of the PAN fiber can be attained and held.

[24] Alternatively, the manifold may have one or more large openings in its upper surface to receive fibers, and one or more larger interior spaces in the manifold through which the fibers are passed while being cooled by indirect heat exchange with the fluid.

[25] Another suitable design would include an integrated spinneret and cooling unit rather than two separate pieces of equipment. In such a design, fibers exiting a spinneret would pass through an integrated cooling unit, which may include tubes or larger openings for the fibers to pass through, a shell for the cooling fluid, and an exit opening or openings for the cooled fibers.

[26] At their optimum handling temperature for tensilizing, the formed filaments pass from the tempering manifold into an enclosed chamber heated to that attained in the manifold. Upon entering the heated chamber, a series of godet rolls would capture the fibers and tensilize them by having each roll rotating at a faster rate than the preceding roll. The number of fibers per roll is a decision made by the fiber producers regularly, everywhere fibers are produced. It is common in the acrylic fiber industry for spinnerets to have 150,000 orifices or more, from which the filament forming resin/solvent solution exits.

[27] Alternatively, the atmospherically controlled chamber into which the newly formed filaments would proceed from the spinneret may be a simple oven-like unit. Its climate (temperature and EC vapor content) under strict control prevents the surface of the filaments from drying out too rapidly, and thereby allow full freedom of the EC within the filaments to pass through to the exterior of such filaments' surface. Under such conditions, the melt flow capability of the PAN melt can replace any minute EC exit tunnels caused by the volatilization of such EC from the filaments.

[28] Optimally, to reduce the fibril temperature efficiently and at a low cost, a manifold or custom-sized and matched air chamber is made and installed just under the spinneret, and fastened to it mechanically. The cooling unit is leak-proof around the spinneret, but is

custom matched to the underside of the spinneret in such a way that the holes from the spinneret from which the fibrils exit it, line up with corresponding holes in the manifold and the fibers pass directly through the cooling unit. The air space inside the cooling unit may be as small as an inch or so wide from top to bottom, or may be larger, as convenient and appropriate. Preferably the manifold is attached to the spinneret so that the direction of flow of the formed fibrils is straight downwards rather than horizontally or upwards.

[29] Processed clean filtered air from an outside supply source which can be adjusted in temperature to better comply with varying fibril thicknesses, is introduced into the manifold at several locations in order that the temperature be uniform throughout the manifold.

[30] Figure 1 is a diagram showing an appropriate cooling manifold for use in the process of this invention. In that figure, a cooling manifold 2 having holes (not shown) through which the fibers may pass is directly and precisely attached to the outlet side of a spinneret 1 in such a way that the holes in the manifold match those in the spinneret. Air or another cooling medium is introduced into the manifold via inlets 3, sized and arranged to provide an even distribution of the cooling medium within the manifold, and is removed via outlets (not shown) situated on the same or on the opposite side of the manifold. Fibers 4 exit from the lower end of the manifold, ready to be tensilized, spooled, etc. downstream.

[31] At the operating temperature of the cooler, the EC plasticizer volatilizes actively. The EC vapors also assist in keeping the exterior surfaces of the fibrils EC-moist, which assists in allowing freedom for EC from the core of the fibril to escape through the outside of the fibril surface by the higher pressure from the fibril inside, due to heat.

[32] The exit of the fibrils from the cooler is through a slot across the bottom surface of the cooler, so that the fibrils pass in neat order as produced in the spinneret. The row or other configuration of fibrils cooled in such way as this is picked up by conventional means and prepared for spooling for downstream secondary operations to suit the producer.

[33] The filaments exit the first tensilizing chamber and enter a similar tensilizing oven heated to 140 - 165°C (284F - 329°F) for further tensilizing. At this temperature range, the chain extender cross-linking agent within the polymer is activated. They impart the higher molecular weight and tensile properties discussed above, by the intertwining of the molecular chains within the polymer, as well as their propagation and the creation of crystalline domains within the polymer.

[34] A third stage tempering oven would complete the total removal by volatilization of any residual EC vapors from the tensitized PAN fibers, using temperatures to about 204°C (400°F).

[35] At this point in the overall process, the filaments are ready for standard high-speed spooling operations. Having been tensitized, thinned to the desired diameter, free of the EC fugitive plasticizer, and with the molecular chains reaching a propagation to 230,000, these filaments have excellent tensile properties for further downstream secondary operations, including oxidization and carbonization in the production of very high quality PAN carbon fibers.

WHAT IS CLAIMED IS:

1. In a process for the production of polyacrylonitrile fibers from a polyacrylonitrile polymer, wherein a polyacrylonitrile polymer that comprises 90 weight percent or more polyacrylonitrile, optionally mixed with from about 30 to about 50 weight percent, based on the weight of the polymer, of a fugitive plasticizer, is heated, provided to an extruder in liquid form, and extruded to form polyacrylonitrile fibers, the improvement comprising,

cooling the fibers, immediately after the extrusion, to a temperature of from about 110 to about 135° C.

2. A process according to claim 1 wherein the polyacrylonitrile polymer contains a chain extender-cross linking agent.

3. A process according to claim 1 wherein the fugitive plasticizer is ethylene carbonate.

4. A process according to claim 1 wherein the cooling is conducted at a temperature of about 120°C.

5. A process according to claim 1, further comprising carbonizing the polyacrylonitrile fibers.

6. A process according to claim 1 wherein the cooling is conducted in an air-cooled manifold that is attached to, and in flow connection with, the extruder.

7. A process according to claim 1 in which the cooling is conducted in a manifold that is attached to, and in flow connection with, the extrude, the manifold being cooled by a liquid cooling agent selected from water, oil, and specialty coolants.

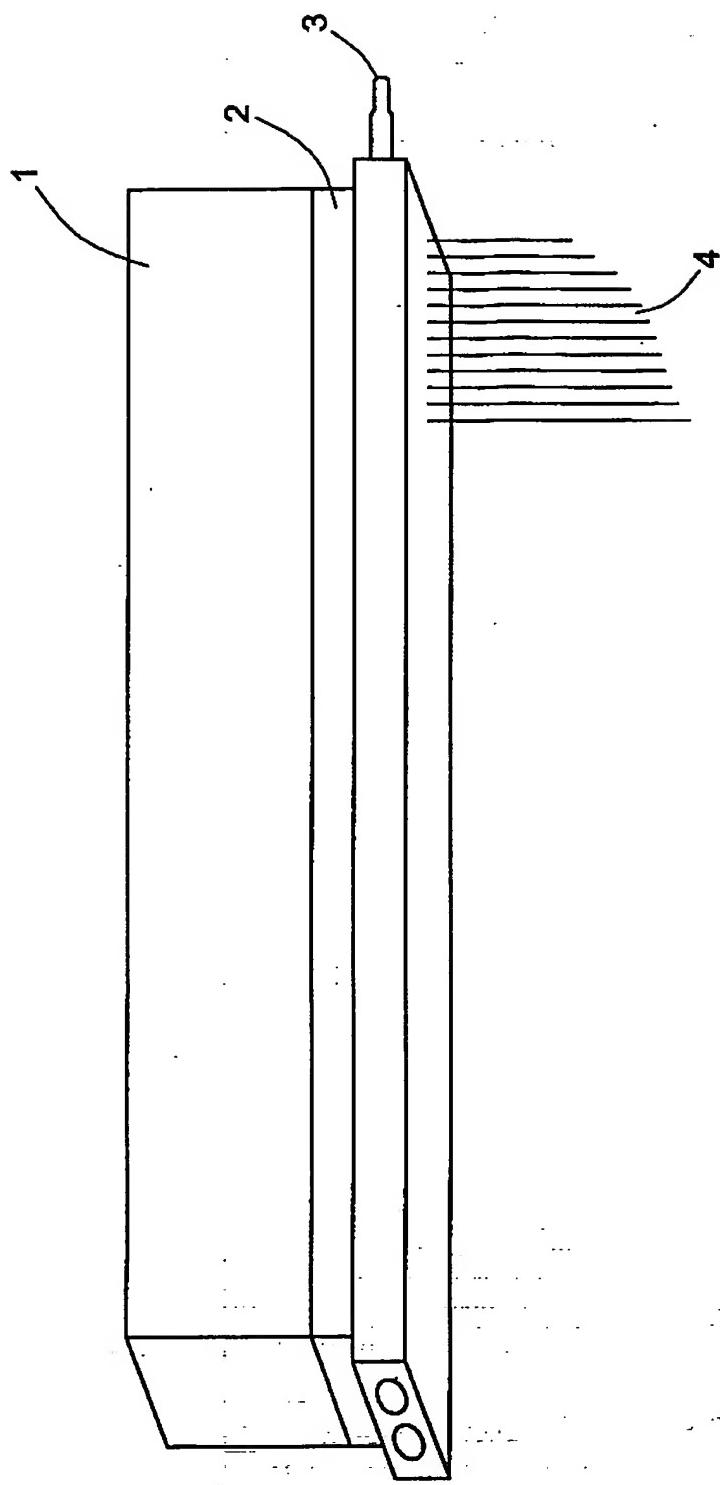
8. A process according to claim 1 wherein the polyacrylonitrile polymer is produced by a melt fusion process.

9. Apparatus for cooling polymeric fibers produced by extrusion, by indirect heat exchange with a cooling medium, comprising:

- (a) a plurality of fiber inlet openings sized and arranged so as to match openings through which the fibers are extruded;
- (b) a plurality of tubes connected to the plurality of fiber inlet openings, sized for passage of fibers therethrough;
- (c) a shell surrounding the plurality of tubes;
- (d) inlet and outlet means in the shell, for introducing thereto and removing therefrom a fluid heat exchange medium, whereby the fluid heat exchange medium is passed in indirect heat exchange with fibers passing through the plurality of tubes; and
- (e) outlet means for removing fibers from the apparatus.

10. Integrated apparatus for extruding fibers and for cooling the extruded fibers, comprising

- (a) an extruding section wherein fibers are extruded from a liquid polymeric material introduced therewith;
- (b) a cooling section located directly below the extruding section for receiving and cooling the extruded fibers;
- (c) inlet means in the cooling section for introducing extruded fibers therewith;
- (d) passage means for passing the fibers through the cooling section;
- (e) a shell surrounding the passage means;
- (f) inlet and outlet means in the shell, for introducing thereto and removing therefrom a fluid heat exchange medium, whereby the fluid heat exchange medium is passed in indirect heat exchange with fibers passing through the cooling section; and
- (g) outlet means for removing the fibers from the cooling section.

*Fig. 1*

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US02/23507

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) B29C 47/88; D01F 6/18

US CL : 264/182, 211.12, 211.18

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 264/182, 211.12, 211.18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A         | US 6,143,411 A (FERGUSON) 07 November 2000.  | 1-9                   |
| A         | US 5,304,590 A (MERZ et al) 19 April 1994.   | 1-9                   |
| A         | US 5,156,831 A (FAIN et al) 20 October 1992.                                       | 1-9                   |
| A         | US 4,681,911 A (CHANG) 21 July 1987.   | 1-9                   |

Further documents are listed in the continuation of Box C.  See patent family annex.

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|---|-----|--|
| • Special categories of cited documents:  | "T" | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  |
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| Name and mailing address of the ISA/US<br>Commissioner of Patents and Trademarks<br>Box PCT<br>Washington, D.C. 20231<br>Facsimile No. (703) 308-5230 | Authorized officer<br><br>BERNARD LIPMAN DEBORAH TAYLOR<br>PAR-LEGAL STAFF LIST <i>Sax</i><br>Telephone No. (703) 308-0661 |